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Electronic transport measurements are a method of obtaining quantitative data about a semiconductor material. The measurement of the conductivity and Hall mobilities and the subsequent analysis can determine the important processes limiting the materials usefulness. For the case of Cadmium Germanium Diarsenide (CGA), saturation at higher pump power in laser systems limits its usefulness as an optical parametric oscillator (OPO) and frequency doubler. The observed saturation has been attributed to inter- and intra-valance band transitions. The intent of the this program was to verify these saturation mechanisms using an appropriate model of CGA valance band structure and electronic transport properties to predict related optional absorption and saturation. Modeling the transport properties of CGA should help in an understanding of the mechanisms behind this saturation. In addition, it will assist in materials improvement programs to reduce or eliminate the process(es) resulting in the observed saturation to obtain high conversion efficiencies observed at short wavelength infrared to LWIR $CO_2$ region. The ultimate goal will be a greater than 25% conversion efficiency with high power $CO_2$ pumps.

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# FINAL REPORT

December 4, 1998

# CHALCOPYRITE MATERIALS MODEL--CM$^2$
## (Electronic Structure and Transport Properties)

AFOSR Contract Number: F49620-96-1-0318

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Electronic transport measurements are a method of obtaining quantitative data about a semiconductor material. The measurement of the conductivity and Hall mobilities and the subsequent analysis can determine the important processes limiting the materials usefulness. For the case of Cadmium Germanium Diarsenide (CGA), saturation at higher pump power in laser systems limits its usefulness as an optical parametric oscillator (OPO) and frequency doubler. The observed saturation has been attributed to inter- and intra-valance band transitions. The intent of the this program was to verify these saturation mechanisms using an appropriate model of CGA valance band structure and electronic transport properties to predict related optional absorption and saturation. Modeling the transport properties of CGA should help in an understanding of the mechanisms behind this saturation. In addition, it will assist in materials improvement programs to reduce or eliminate the process(es) resulting in the observed saturation to obtain high conversion efficiencies observed at short wavelength infrared to LWIR $CO_2$ region. The ultimate goal will be a greater than 25% conversion efficiency with high power $CO_2$ pumps.

As a result, it is expected that the long wavelength range will be extended to a useful high power second harmonic generation in CGA to the 8-12 micron range for use with $CO_2$ laser pumps. This will enable the development of agile infrared mid-band high power laser systems for defense against heat seeking missiles.

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The transport model is complicated in the fact that there are multiple scattering mechanisms active at similar temperatures that must be accounted for correctly. Along with this the band structure must be included and the solution of the Boltzmann equation must be treated very carefully. The band structure for most semiconductors is very complicated and must be solved numerically in order to account for the nonparabolicity and anisotropy of the valence bands. The inclusion of the band anisotropy and nonparabolicity in the treatment of the scattering mechanisms will yield significant effects in the calculation of the mobilities. This allows for the calculation of the nonequilibrium distribution function to be calculated to orders beyond the relaxation time approximation exactly.

The band structure near the center of the Brillouin zone for CGA was determined using the 8x8 **k•p** Kane model[1] to include the effects of the remote bands. Remote bands are defined as any band outside the lowest conduction band and upper most valence bands to include the spin-orbit split-off band. CGA has the chalcopyrite structure, which can be treated as a zinc blende with an applied strain. This results in a splitting of the heavy and light hole valence bands. From this model the density of states can be determined and the "density-of-states effective mass" is calculated[2]. Using the density-of-states effective mass the carrier concentration effective mass[2] is also determined. Both of these are used in the calculation of the conductivity and Hall mobilities. In a personal communication from Prof. Yu Rud[3], theoretical band edge effective masses have been obtained and are included in Table 1 along with our effective masses.

| Valence Band | ∥ c-axis | ⊥ c-axis |
|---|---|---|
| $V_1$ | 0.02 (0.029) | 0.03 (0.020) |
| $V_2$ | 0.34 (0.41) | 0.09 (0.06) |
| $V_3$ | 0.16 (0.19) | 0.10 (0.09) |

Table 1: Band edge effective masses for CGA

( )-Theoretical values from S. I. Borisenko, Candidates Thesis, "Analysis of the many electrical and optical properties of II-IV-$V_2$ diamond semiconductors", V. V. Kuybishev State University, Tomsk, Russia (1986).

The theoretical values supplied by Prof. Rud indicate that the CGA may be modeled using Indium Arsenide (InAs) experimental parameters. This indicates promise

because InAs is a III-V analog of the pseudo III-V compound CGA. Figure 1 shows the energy band structure of CGA near **k** = 0 (the center of the Brillouin zone).

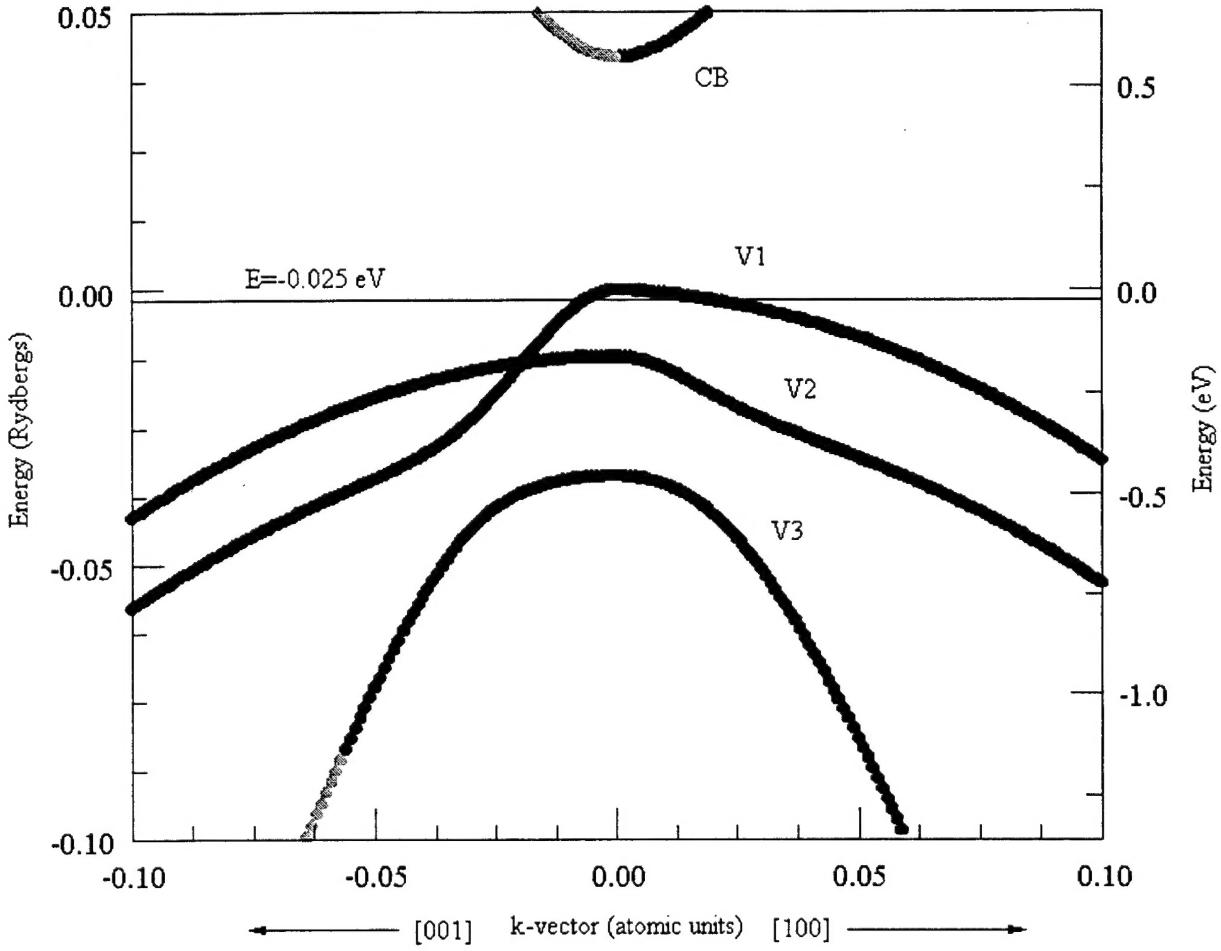


Figure 1: Energy dispersion for k parallel and perpendicular to the c-axis [001] in Cadmium Germanium Diarsenide.

Phonon scattering plays an important part in determining the electrical properties of semiconductors. In semiconductors without inversion symmetry, four types of lattice scattering are present. These are acoustic, piezoelectric, polar and nonpolar optical scattering. Acoustic phonon scattering is dominant at low temperatures.

Piezoelectric scattering is a second order mechanism related to strain produced by an acoustic phonon propagating in crystals having no inversion symmetry. This oscillatory strain produces an electric polarization, proportional to the strain, which interacts with the charge carrier.

Optical phonon scattering becomes significant at temperatures above liquid nitrogen and may be of great importance in the determination of the OPO saturation in CGA. CGA has 8 atoms per unit cell; which leads to 24 phonon modes. Three of these modes are acoustic modes and the other 21 are optical modes. The phonon modes have been measured and the appropriate symmetry properties have been determined[4,5].

Madarasz and Szmulowicz[6] were the first to incorporate the nonparbolicity of the band structure into the calculation of hole-acoustic phonon transition rates for silicon. Tiersten[7] incorporated the anisotropy of the acoustic spectrum into his calculation of transition rates but used parabolic bands. The acoustic phonon velocities and polarization modes have been measured and the elastic coefficients determined for CGA. This information has been incorporated into a computer code which allows the calculation of hole-acoustic phonon transition rates including both the anisotropy of the phonon velocities and the anisotropy and nonparbolicity of the band structure. This has been done to do as complete a job as possible given the lack of experimental data in this regard. Figure 2 shows a plot of the hole-acoustic phonon transition rates for forward directions along high symmetry directions.

In order to calculate the mobilities, the hole-phonon scattering data has been fit to a double set of "Tetragonal Harmonics". The "Tetragonal Harmonics" are a set of polynomials that have the symmetry of the $D_{2d}$ group. At this time hole-phonon transition rates can be fit to a sum of the incident and scattered angular momentum to $l + l' = 8$, although it may not be necessary to use that many terms. The convergence of the fitting coefficients will determine how many orders of angular momentum will be needed in the transport calculation.

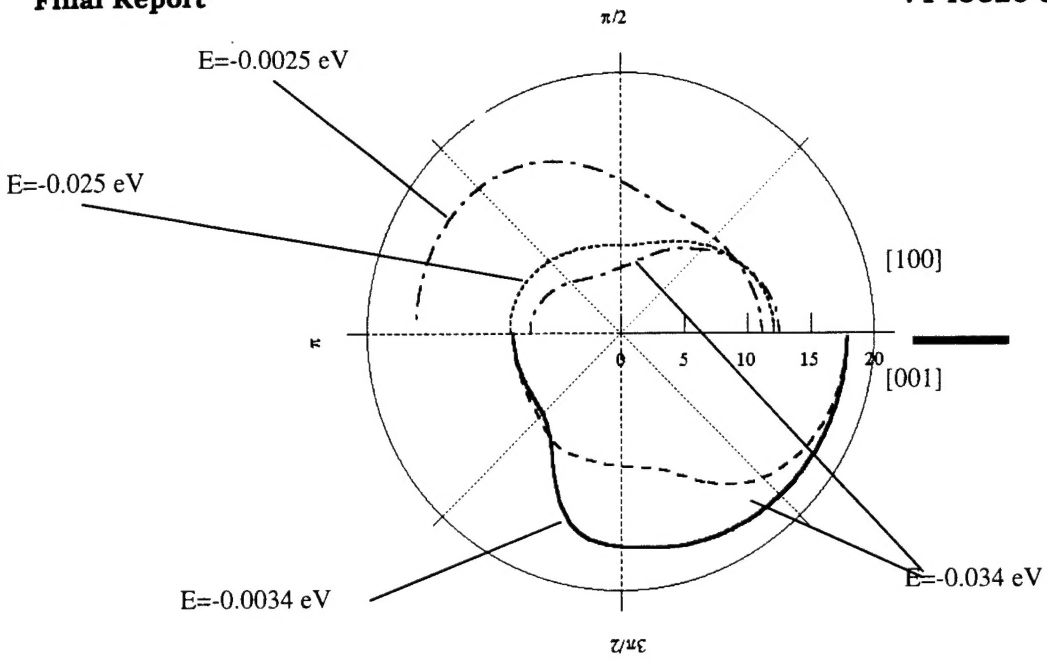


Figure 2: Angular plot of hole-acoustic phonon scattering rates which shows the energy and angular dependence .

The theory of transport for materials with tetragonal symmetry has been developed although the computer code has not been fully implemented as of yet. The theory has been developed keeping in mind that there will be different conductivity and Hall mobilities in directions parallel and perpendicular to the c-axis of the crystal. A symmetry analysis also shows that three distinct calculations must be made to accurately determine the conductivity and Hall mobilities[8]. This indicates that the calculation must be done systematically altering the orientation of the applied electric and magnetic fields over three unique orientations to determine the differences between the calculated conductivity and Hall mobilities. The calculation utilizes the fitting parameters from the hole-phonon scattering rates in an exact calculation of the conductivity and Hall mobilities beyond the relaxation time approximation. The ratio of the Hall mobility to the conductivity mobility is the r-factors (there are two in this case, one parallel to the c-axis and one perpendicular to the c-axis) and will be calculated. The r-factors will be used to obtain hole concentrations. The charge balance equation in conjunction with the hole-concentration data will then be used to calculate acceptor activation energies. As with prior codes written for this project, codes are developed for silicon and the results verified against previously published data. Only then are the codes expanded to model CGA. Again, limiting cases are taken to model InAs and other III-V compounds to ensure the accuracy and validity of the codes.

To complete the model the several scattering mechanisms must be added. The formalism for the hole-optical phonon transition rates has been set up. These rates must be fitted to the tetragonal harmonics and integrated into the general scattering integral operator of the Boltzmann equation. Similar work needs to be done for ionized impurity scattering. The general formalism for the solution of the Boltzmann equation has been set up and the code is presently being written. The final step is to calculate the conductivity and Hall mobilities, and hole carrier concentrations over the full range of temperatures in a parametric study of dopant/compensation levels and correlate this with experimental data.

The student, Mr. Dan Northem, continues to work on this project as his Ph.D. thesis. It is expected by late spring of '99 that he will be able to generate phonon-limited mobilities, which should prove sufficient for the completion of his Ph.D. work. It was hoped that there would be continued funding of the project. Funding sufficient enough to assisted the student in finishing his degree work and allow for a one year post-doctoral position enabling him to finish the full mobility calculation and then progress onto to the calculation of the nonlinear absorption using the knowledge and transition rates developed in the transport calculation. Unfortunately, this will not happen and the project will not benefit from whatever progress that can be made from this point on. The student, Dr. John Dimmock and I have invested considerable time and effort in breaching a new field, defining the problem(s) of relevance to the Air Force and moving towards a solution. All will be for naught because of the lack of funds to support approximately one and one half-man years more.

Frank L. Madarasz 12/4/98

Frank L. Madarasz Date

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